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Core-valence coupling in the Ru $4p$ photoexcitation/Auger decay process: Auger-photoelectron coincidence spectroscopy study

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The $N_{23}VV$ Auger spectrum of Ru has been measured in coincidence with $4p_{1/2}$ and with $4p_{3/2}$ photoelectrons. Unlike other metals that exhibit bandlike Auger decays, we find that the two Auger spectra are not shifted by the difference in core level binding energies. A consistent description of these transitions and the core level line shape requires consideration of the relativistic multiplet splitting in the intermediate core hole state and two-valence-hole Auger final state. The results suggest that the large linewidth of the $4p$ levels is primarily due to multiplet splitting, and that an $N_2(N_3N_{45})N_{45}N_{45}$ super-Coster-Kronig transition is only a minor decay channel.

The intrinsic line shapes of core-valence-valence (CVV) Auger transitions in solids contain valuable information about the local density of states (LDOS) and electron-electron correlations in the valence band. As such, a detailed understanding of CVV Auger spectra can offer considerable insight into the electronic properties of solids as well as into the nature of the photoexcitation and decay process. In the late $4d$ transition metals, the $N_{23}VV$ Auger spectra associated with decay of the shallow $4p$ holes are particularly interesting for several reasons. In conventional photoemission spectra, the $4p$ core levels have unusually large line widths attributed to a rapid Auger decay of the core hole.[1,2] This gives rise the interesting situation where core hole decay occurs on a short time scale that is competitive with screening, shake-up, and even shake-down processes.[3] Furthermore the line shapes of the core level and Auger spectra suggest the presence of a significant super Coster-Kronig decay channel. However, determining the intrinsic line shapes of these transitions using conventional spectroscopic techniques is problematic for at least three reasons. First, the N_2VV and N_3VV spectra overlap in energy.[2] Secondly, any lifetime width of the core hole state will further broaden the Auger spectra. Finally, owing to their low kinetic energy, the Auger features reside on a large secondary electron background.[1,2,4]

In this paper, we present Auger-photoelectron coincidence spectra (APECS) of the Ru $N_{23}VV$ Auger transitions measured in coincidence with Ru $4p_{3/2}$ and with Ru $4p_{1/2}$ photoelectrons. To provide a consistent understanding of these two spectra and the line shapes of the core levels, we have performed a fully relativistic Dirac-Fock (DF) calculation[5–7] of the states involved in the photoexcitation/Auger decay process. Experimentally, we find that the coincidence N_3VV and N_2VV Auger transitions have line shapes that cannot consistently be described in terms of a self-convolution of the valence band density of states, even when distorted by valence-valence correlations. Furthermore, the

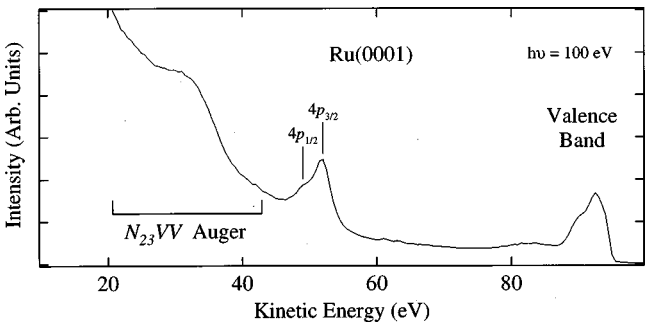

FIG. 1. Wide energy scan singles photoemission spectrum from Ru(0001) obtained at $h\upsilon = 100$ eV.

energy shifts and intensities in the spectra indicate that super-Coster-Kronig transitions cannot be responsible for the observed line shapes. To obtain a good description of both Auger spectra and the core level line shape from a single theory requires considering the multiplet configurations of the intermediate core hole states and the Auger two-hole final states as given by the relativistic DF calculations. These results show that even for a relatively light $4d$ transition metal such as Ru, strong angular momentum coupling and relativistic effects must be included to account for its excitation and decay spectra.

The APECS data were obtained at the vacuum ultraviolet (VUV) storage ring of the National Synchrotron Light Source (NSLS) on beam line U14A. Detailed descriptions of the experimental setup and the basic principles of APECS are presented elsewhere.[8,9] Briefly, the instrumentation consisted of an ultrahigh vacuum chamber housing two cylindrical mirror analyzers (CMA's) focused on the same spot on the sample, which was illuminated by monochromatized synchrotron radiation ($h\upsilon = 140$ eV, unless otherwise stated). Coincidence N_3VV (N_2VV) Auger spectra were acquired by scanning one CMA through the Auger region and only accepting counts that arrive in time coincidence with those from the second CMA that was set to a fixed energy associated with Ru $4p_{3/2}$ ($4p_{1/2}$) core level photoelectrons. In all cases, a conventional (also called singles) spectrum was acquired simultaneously with the coincidence data. The overall resolution (electron plus photon) in each spectrum was ~0.8 eV. All kinetic energies are referenced to the vacuum level (E_V). The sample, a Ru(0001) single crystal, was prepared by repeated cycles of sputtering and oxygen exposure to a temperature of 1600 K. Sample cleanliness was evaluated by monitoring the shape of the electron excited Auger spectrum, as well as the shape of the valence band in photoemission. After ~30 min in the background pressure of 1×10^{-10} Torr, a small feature (most likely associated with CO or H adsorbed from the residual gas) could be detected in the photoemission spectrum. To eliminate possible complications from contamination, measurements proceeded in repeated cycles of data acquisition for 20 min followed by flashing the sample to 1900 K.

A wide scan photoemission spectrum from the Ru(0001) surface excited by 100 eV photons is shown in Fig. 1. As noted above and similar to other members of the late $4d$ transition metal series,[1,10,11] the $4p$ core level is a very broad spectral feature. In the Auger region of the spectrum, we note that the spectral weight of the $N_{23}VV$ transition is concentrated towards low kinetic energies. This lack of intensity in the N_2VV portion of the spectrum has been attributed to an $N_2(N_3N_{45})N_{45}N_{45}$ super-Coster-Kronig (SCK) process that provides an extra decay channel. In this transition, a $4p_{1/2}$ core hole first hops to the $4p_{3/2}$ level, creating an electron-hole pair excitation in the valence band, and then the $4p_{3/2}$ hole subsequently decays via a CVV process.[1,2] As shown below, in systems where the CVV Auger spectra from the different components overlap, caution must be used when interpreting line shapes in conventional Auger spectroscopy.

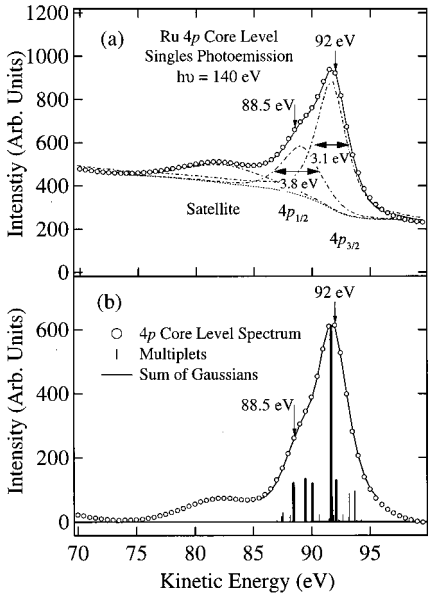

FIG. 2. (a) Singles Ru $4p$ core level spectrum obtained at $h\upsilon = 140$ eV. The solid line is an attempt to account for the core level spectrum with Lorentzians centered at 91.5 and 89 eV, and the satellite feature by a Gaussian centered at 83 eV. Notice that the 89 eV line is only 20% broader than the 91.5 eV line. (b) The background-subtracted Ru $4p$ core level spectrum. The bars indicate different atomic state functions (ASF's) representing the $4p^5 4d^8$ configuration with relative intensities given by the Dirac-Fock calculation. The heavy bars are the ASF's used as initial states for the calculated Auger lines in Fig. 3. The solid line is the sum of Gaussians with 1 eV widths whose heights and energy locations are determined by the bar plot.

A singles photoemission spectrum of the Ru $4p$ core level region obtained with 140 eV photons and plotted on a smaller energy scale, is shown in Fig. 2(a). In addition to the core level feature, a broad peak is seen centered at 83 eV. This satellite feature is associated with the occurrence of additional valence band excitations generated in the core level photoexcitation process and is discussed elsewhere.[3] An attempt to fit the $4p$ line shape with two Lorentzians to account for the spin-orbit split $4p_{3/2}$ and $4p_{1/2}$ core levels, and a Gaussian for the satellite, is given by the solid line. An additional width of 0.7 eV for the $4p_{1/2}$ line is required to maintain the statistical ratio of 2:1 for the $4p_{3/2}$ to $4p_{1/2}$ intensities. In previous studies, this additional width was taken as further evidence of the $N_2(N_3N_{45})N_{45}N_{45}$ SCK decay.[1,2] On the other hand, theoretical studies find a larger width for the $4p_{1/2}$ level even though they do not include an SCK transition.[10,11]

The Ru $N_{23}VV$ Auger spectra obtained in coincidence

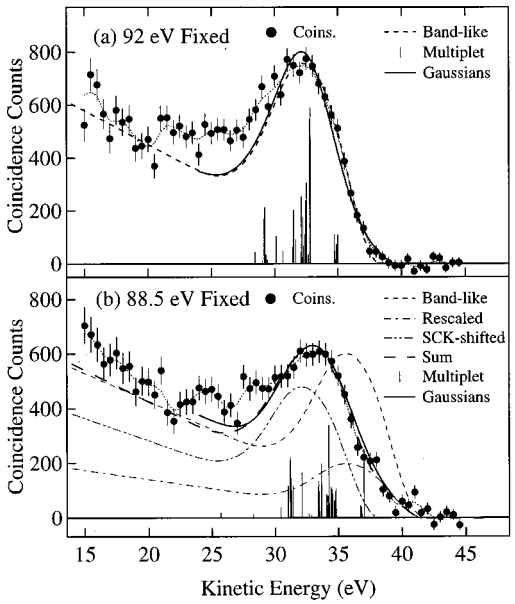

FIG. 3. (a) The Ru $N_{23}N_{45}N_{45}$ Auger spectrum obtained in coincidence with $4p$ photoelectrons emitted at 92 eV. The dotted curve is a smooth line to the experimental points (filled circles). The dashed curve is an attempt to describe the spectrum by a bandlike Auger decay. The vertical bars indicate the multiplets of the Ru $4p^6 4d^6$ configuration and the solid curve is the sum of Gaussians with 2 eV widths whose heights and energy locations are determined by the bar plot. (b) Same as (a) but in coincidence with photoelectrons emitted at 88.5 eV. The heavy dashed curve illustrates that an acceptable description of the experimental data would require 80% of the $4p_{1/2}$ core holes to decay via a super Coster-Kronig process (dash-double dotted curve) and 20% direct decay (dash-dotted curve).

with photoelectrons at 92 eV (nominally Ru $4p_{3/2}$) and 88.5 eV (nominally $4p_{1/2}$) are presented in Figs. 3(a) and 3(b), respectively. Immediately, these two spectra illustrate several important advantages of APECS over conventional spectroscopy. First, the large background under the singles Auger spectrum of Fig. 1 is eliminated. Second, the intensity at low kinetic energies is also significantly reduced. This is because of the substantial reduction of the extrinsic inelastic background in coincidence. We infer that much of the remaining background is intrinsic and related to more complicated nonradiative decay modes. Finally, and most importantly for this study, the spectra in Figs. 3(a) and 3(b) are surprisingly *similar*, with the N_2VV spectrum peaking at only slightly higher energy despite the fact that the coincidence electron energies differ by almost 3.5 eV.

The dashed curve in Fig. 3(a) is an attempt to fit the Ru N_3VV spectrum with the sum of a self-convolution of the valence band density of states (SCDOS) and a linear background. This curve models a bandlike Auger decay where no significant correlations between the two final state holes is present in the valence band. The curve gives a good description of this spectrum at high kinetic energies. The intensity at kinetic energies below ~30 eV is somewhat underestimated, possibly owing to our choice of background. In contrast, the same approach gives an unsatisfactory description of the N_2VV line shape, as seen by the dashed curve in Fig. 3(b). The calculated spectrum greatly overestimates the spectral weight above 35 eV, and underestimates it at lower energies. Although the experimental spectrum shows some intensity near 41 eV (the independent electron cutoff for N_2VV emission), the data does not acquire appreciable intensity until ~37 eV. Furthermore, the calculated curve has a maximum near 36 eV while the data peaks at a much lower energy, near 33 eV.

The primary observation from Fig. 3(b) is that spectral weight in the data is shifted to significantly lower kinetic energy as compared to the SCDOS. It is well known that electron-electron correlation effects in the valence band can produce such an effect. For a solid with correlation energy $\mathcal{U}$ in a valence band of width W, spectral weight in the CVV line shifts to lower kinetic energy as $\mathcal{U}/W$ approaches unity.[12–15] However, since both the N_2VV and the N_3VV transitions leave two holes in the valence band, this effect does not explain why spectral weight is shifted to lower kinetic energy in the N_2VV line but not in the N_3VV line. Similarly, matrix element effects, i.e., different matrix elements for valence band states of different orbital character, are expected to influence both transitions in a similar way and cannot account for the observed differences between the two spectra.

Another possible explanation for the similarity of the N_2VV and N_3VV spectra is that an $N_2(N_3N_{45})N_{45}N_{45}$ SCK transition is a significant decay channel in this system.[1,2] As this channel is only available for a $4p_{1/2}$ core hole, such a transition could shift spectral weight in the N_2VV spectrum while leaving the N_3VV Auger line unaffected. However, as we show here, this idea cannot consistently account for the line shapes of the Auger transitions and the $4p$ core levels. First, if the electron-hole pair generated by the SCK transition remains in the region of the excited atom, the spectral weight from the subsequent $4p_{3/2}$ core hole decay is expected to be shifted to lower energy.[15] Comparing Figs. 3(a) and 3(b) we see that the N_2VV peak is actually ~1 eV *higher* kinetic energy than the N_3VV spectrum, suggesting that this sort of decay is not present. On the other hand, if the electron-hole pair relaxes prior to decay of the $4p_{3/2}$ core hole, the SCK contribution to the N_2VV spectrum would have the same line shape as the N_3VV spectrum. Therefore, the direct channel would be modeled by an unshifted SCDOS as given by the dot-dashed curve in Fig. 3(b). The intensity attributed to this channel is limited by the high-energy edge of the data. The contribution from the SCK channel would be given by the SCDOS shifted down by the energy separation between the $4p_{1/2}$ and $4p_{3/2}$ core levels as shown by the double-dot-dashed curve in Fig. 3(b) and would account for the remaining intensity. This procedure gives a reasonable fit to the data, [heavy dashed line in Fig. 3(b)] but requires that the branching ratio between the SCK preceded and the direct CVV decay paths that is ~4:1. Such a large SCK decay channel would result in a similar ratio of 4:1 in the $4p_{1/2}$ to $4p_{3/2}$ line widths. However, from Fig. 2(a) we find that the core level data is described by a ratio of only ~1.2:1 ratio. So this approach also has significant difficulty reconciling the line shapes of both the core level and the Auger spectrum.

In order to understand core hole excitation and decay in this system and to consistently explain the line shapes of the N_2VV and N_3VV spectra from a common perspective, we

have performed an atomic Dirac-Fock calculation.[5–7] Each atomic state function (ASF), whose whole set constitutes the multiplet structure, is a linear combination of configuration state functions (CSF) having the same parity, total angular momentum, and angular momentum projection. Each CSF is described by a linear combination of Slater determinants and multiplet structure theory. The $4p^5 4d^8$ and $4p^6 4d^6$ electronic configurations have been used to represent the intermediate core hole state and two-hole final state of the process, respectively. We therefore assume that the core hole is fully screened by a d electron.[16]

The ability of this approach to describe the intermediate core hole state is demonstrated in Fig. 2(b). Here, the background-subtracted core level spectrum is compared to a sum of Gaussians with 1 eV full width half maximum (FWHM), given by the solid curve. The energy and intensity of each Gaussian is given by an ASF of the DF calculation, and is indicated by the bar plot. Clearly, the multiplet structure predicted by the DF calculation gives a very satisfactory description of the core hole excitation spectrum.

The heavy bars in Fig. 2(b) indicate the major lines sampled in the photoelectron channel for the two fixed energies at which we obtained the Auger spectra of Fig. 3. The bar plots in Figs. 3(a) and 3(b) represent the Auger final states reached from these lines. The energy separation and relative intensity of these lines have been calculated using the method employed by McGuire[17] and others.[18,19] The solid curve is a sum of Gaussians with FWHM of 2.0 eV,[20] associated to each Auger final state multiplet. We see that these lines account for the major features present in both Auger spectra. In particular, they correctly describe the shift in spectral weight to lower kinetic energy present in the N_2VV spectrum, as well as the intensity near $\sim$37 eV. Even some of the fine structure near 28 eV in the N_3VV spectrum and near 31 eV in the N_2VV spectrum is suggested by the calculation. The additional structure seen at lower energies in both spectra are most likely due to other final state configurations.

There are several important implications of these results. First, despite the apparently bandlike nature of the Auger spectrum observed in singles spectroscopy, the Auger spectrum of Ru cannot be described within an independent electron theory. Angular momentum coupling between the core hole and the open $4d$ shell of the valence band is extremely important in determining the line shapes of both the Auger and core level spectra. These results suggest that this coupling must be taken into account in any attempt to describe the spectral properties of the late $4d$ transition metal series. Moreover, despite their relatively low atomic mass, we find that it is essential to include relativistic effects to obtain a correct description of this system.[3] Regarding the line shape of the $4p$ core level spectrum, the apparent difference in linewidth of the $4p_{1/2}$ and $4p_{3/2}$ levels is not evidence for a super Coster-Kronig decay of the $4p_{1/2}$ level. The core level line shape is well described by the DF calculation. The SCK transition, if it exists at all, is only a minor decay channel. We conclude that the width of the core level spectrum is primarily caused by multiplet splitting of the intermediate core hole states rather than lifetime broadening owing to rapid Auger decay of the core hole. This is very different from the closed d-shell systems of Cu and Ag where line narrowing using APECS has conclusively shown[21,22] that the large linewidths of the shallow p levels are due to lifetime broadening.

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[1] R. Nyholm and N. Martensson, Chem. Phys. Lett. **74**, 337 (1980).

[2] N. Martensson and R. Nyholm, Phys. Rev. B **24**, 7121 (1981).

[3] R. Gotter, R. A. Bartynski, S. L. Hulbert, H. Nozoye, and M. Zitnik, J. Electron Spectrosc. Relat. Phenom. **93**, 201 (1998).

[4] E. Jung, H. Q. Zhou, J. H. Kim, S. Starnes, R. Venkataraman, and A. H. Weiss, Appl. Surf. Sci. **116**, 318 (1997).

[5] R. Gotter, R. A. Bartynski, S. L. Hulbert, X. Wu, H. Nozoye, and M. Zitnik, J. Electron Spectrosc. Relat. Phenom. **93**, 201 (1998).

[6] I. P. Grant, J. Phys. B **7**, 1458 (1974).

[7] K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plumer, Comput. Phys. Commun. **55**, 425 (1989).

[8] E. Jensen, R. A. Bartynski, S. L. Hulbert, and E. D. Johnson, Rev. Sci. Instrum. **63**, 3013 (1992).

[9] R. A. Bartynski, E. Jensen, and S. L. Hulbert, Phys. Scr. **41**, 168 (1992).

[10] M. H. Chen, B. Craseman, L. I. Yin, T. Tsang, and I. Adler, Phys. Rev. A **13**, 1435 (1976).

[11] E. McGuire, Phys. Rev. A **9**, 1840 (1974).

[12] M. Cini, Solid State Commun. **20**, 605 (1976).

[13] M. Cini, Solid State Commun. **24**, 681 (1977).

[14] G. A. Sawatzky, Phys. Rev. Lett. **39**, 504 (1977).

[15] G. A. Sawatzky, in *Auger Electron Spectroscopy*, edited by C. L. Briant and R. P. Messmer (Academic, Boston, 1988).

[16] G. G. Kleinman, R. Landers, P. A. P. Nascente, and S. G. C. de Castro, Phys. Rev. B **46**, 4405 (1992).

[17] E. J. McGuire, in *Atomic Inner-Shell Processes*, edited by B. Crasemann (Academic, New York, 1974).

[18] G. Cubiotti, A. D. Laine, and P. Weightman, J. Phys.: Condens. Matter **1**, 7723 (1989).

[19] J. A. Evans, A. D. Laine, P. Weightman, J. A. D. Matthew, D. A. Wolf, D. I. Westwood, and R. H. Williams, Phys. Rev. B **46**, 1513 (1992).

[20] Owing to the instrumental resolution of two CMA's and the two-hole lifetime, the Gaussian width for multiplets in the Auger spectrum is larger than that for the core level spectrum.

[21] E. Jensen, R. A. Bartynski, R. F. Garrett, S. L. Hulbert, E. D. Johnson, and C. C. Kao, Phys. Rev. B **45**, 13 636 (1992).

[22] R. A. Bartynski, Q. Qian, and S. L. Hulbert, J. Phys. I **9**, 157 (1999).